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TECHNICAL REPORT NO. 15

Semiclassical Corrections for

Inelastic Atom-Surface Scattering

from Classical Trajectories

by

W. Kohn, J. H. Jensen, and P. Chang

to be submitted

Department of Physics

University of California, Santa Barbara

Santa Barbara, CA 93106

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Semiclassical Corrections for Inelastic Atom-Surface Scattering from Classical Trajectories (Preliminary draft)

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ABSTRACT: We consider an atom scattered inelastically from a surface and derive a formula for the exact semiclassical limit of the expectation value of an arbitrary, smooth function of the scattered atom's final momentum. The formula expresses this semiclassical limit in terms of equilibrium correlations for the atoms which compose the surface and quantities which can be calculated from classical scattering trajectories. We give numerical results for a simple one-dimensional example and compare these results with those given by the trajectory approximation.

I. Introduction

Atom-surface scattering can be used to obtain information about the structure and dynamics of a surface and about the atom-surface interaction potential.[1] When the initial energy of an incident atom (hereafter called the "incidon") is large and its de Broglie wavelength is small, the semiclassical limit provides an accurate approximation. In this paper, we derive an expression for the exact semiclassical limit of expectation values of functions of the incidon's final momentum in terms of classical trajectories and equilibrium correlations for the atoms composing the surface. Since there are well-established methods for calculating classical trajectories for realistic surfaces,[2] the formula provides a practical method to obtain the semiclassical approximation for quantities observed in scattering experiments.

We illustrate the theory with a one-dimensional model consisting of an incidon scattering off a harmonic oscillator, giving numerical results for the semiclassical momentum shift and momentum uncertainty. We compare these results to those produced by the trajectory approximation which is frequently used in the study of inelastic atom-surface scattering.[3-9] We find that the trajectory approximation does not, in general, give either the correct semiclassical shift or uncertainty. However, if the incidon-oscillator interaction is adiabatic or if the maximum displacement of the harmonic oscillator from its equilibrium position is much smaller than the range of the interaction potential, then the trajectory approximation accurately predicts the momentum uncertainty.

II. Definition of Semiclassical Limit

Many approaches to surface scattering have gone under the name "semiclassical." Often the term means that the approach employs both classical and quantum mechanical methods. Alternatively, semiclassical can imply an expansion in powers of $\hbar$. It is in this latter, more precise sense that we use the word.

We consider a d-dimensional quantum system consisting of an incidon and a surface substrate of harmonic oscillators. The Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}, \xi_i) + \frac{1}{2}\sum_{i=1}^{N}(\sigma_i^2 + \omega_i^2 \xi_i^2), \tag{1}$$

where $\mathbf{p}$ is the incidon's momentum, $\mathbf{x}$ is the incidon's position, m is the incidon's mass, and $V(\mathbf{x}, \xi_i)$ is the atom-surface interaction potential which is taken to be a smooth function of $\mathbf{x}$ and ξ_i. σ_i and ξ_i are coordinates for the normal modes of the surface atoms, obeying the commutation relation $[\xi_i, \sigma_j] = i\hbar\delta_{ij}$, and ω_i is a normal mode frequency. We assume that $V(\mathbf{x}, \xi_i) \to +\infty$ as $\mathbf{x} \cdot \hat{\mathbf{n}} \to -\infty$, and $V(\mathbf{x}, \xi_i) \to 0$ as $\mathbf{x} \cdot \hat{\mathbf{n}} \to +\infty$, where $\hat{\mathbf{n}}$ is a unit vector perpendicular to the surface.

At an initial time, t_0, the surface is in thermal equilibrium at a temperature, $T = \hbar\tau$, and the incidon is described by a wave-packet of the form

$$\psi(\mathbf{x}) = (2\pi\hbar\gamma)^{-\frac{d}{4}} \exp\left[-\frac{(\mathbf{x} - \mathbf{x}_0)^2}{4\hbar\gamma} + i\frac{\mathbf{p}_0 \cdot \mathbf{x}}{\hbar}\right], \tag{2}$$

where $\mathbf{x}_0$ is the incidon's initial mean position and $\mathbf{p}_0$ is its initial mean momentum, satisfying $\mathbf{p}_0 \cdot \hat{\mathbf{n}} < 0$.

At a later time, t, the expectation value of a smooth function, $Q(\mathbf{p})$, is given by

$$< Q(\mathbf{p}) > (t) = Q(t - t_0, \mathbf{x}_0, \mathbf{p}_0, \gamma, \tau, \hbar). \tag{3}$$

Since the impact parameter for the collision is generally unknown, we average $< Q(\mathbf{p}) >$ over the components of $\mathbf{x}_0$ which lie parallel to the plane of the surface. Indicating this average with a subscript a, we have

$$< Q(\mathbf{p}) >_a (t) = Q_a(t - t_0, \mathbf{x}_0 \cdot \hat{\mathbf{n}}, \mathbf{p}_0, \gamma, \tau, \hbar). \tag{4}$$

The final classical value for Q is defined

$$Q_{fc}(\mathbf{p}_0,\tau) = \lim_{\gamma\to\infty}\left(\lim_{\mathbf{x}_0\cdot\hat{\mathbf{n}}\to\infty}\left(\lim_{(t-t_0)\to\infty}\left(\lim_{\hbar\to 0} Q_a(t-t_0,\mathbf{x}_0\cdot\hat{\mathbf{n}},\mathbf{p}_0,\gamma,\tau,\hbar)\right)\right)\right), \tag{5}$$

while the semiclassical shift for Q is

$$\Delta Q(\mathbf{p}_0,\tau,\hbar) = \hbar\lim_{\gamma\to\infty}\left(\lim_{\mathbf{x}_0\cdot\hat{\mathbf{n}}\to\infty}\left(\lim_{(t-t_0)\to\infty}\left(\lim_{\hbar\to 0}\frac{\partial}{\partial\hbar} Q_a(t-t_0,\mathbf{x}_0\cdot\hat{\mathbf{n}},\mathbf{p}_0,\gamma,\tau,\hbar)\right)\right)\right). \tag{6}$$

Finally, we define the semiclassical limit or approximation for Q as $Q_{sc} = Q_{fc} + \Delta Q$.

If the incidon's initial energy is large compared to the energy of a typical phonon and the incidon's de Broglie wavelength is small compared to the distance scale over which the interaction potential varies substantially, then we expect Q_{sc} to be a good approximation for the final expectation value of Q. Since we have taken the surface temperature to be of order $\hbar$, the initial energy must also be large compared to $k_B T$ with k_B being Boltzman's constant.

III. Derivation of Formula for Semiclassical Limit

To obtain an expression for the semiclassical limit, we use the Wigner distribution function[10] defined by

$$f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t) = \int \frac{d^d a D\alpha_i}{(2\pi\hbar)^{(d+N)}} \exp\left[-\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{a} + \sum_{i=1}^{N}\sigma_i\alpha_i)\right] \times \rho\left(\mathbf{x}+\frac{1}{2}\mathbf{a},\mathbf{x}-\frac{1}{2}\mathbf{a},\xi_i+\frac{1}{2}\alpha_i,\xi_i-\frac{1}{2}\alpha_i,t\right), \tag{7}$$

where $D\alpha_i \equiv \prod_{i=1}^{N} d\alpha_i$, and $\rho(\mathbf{x},\mathbf{x}',\xi_i,\xi_i',t) \equiv <\mathbf{x},\xi_i|\rho(t)|\mathbf{x}',\xi_i'>$ is the density matrix. The expectation value of $Q(\mathbf{p})$ can be written

$$< Q(\mathbf{p}) > (t) = \int d^d x d^d p D\xi_i D\sigma_i Q(\mathbf{p}) f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t). \tag{8}$$

The equation of motion for f is

$$\Big(\frac{\partial}{\partial t}+\frac{p_i}{m}\frac{\partial}{\partial x_i}+\sigma_i\frac{\partial}{\partial \xi_i}-\omega_i^2\xi_i\frac{\partial}{\partial \sigma_i}\Big)f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t)=$$
$$\frac{2}{i\hbar}\sum_L J(\mathbf{x},\xi_i,l_i,\lambda_i)\Big[\prod_{j=1}^{d}\Big(\frac{i\hbar}{2}\frac{\partial}{\partial p_{(j)}}\Big)^{l_{(j)}}\Big]\Big[\prod_{k=1}^{N}\Big(\frac{i\hbar}{2}\frac{\partial}{\partial \sigma_{(k)}}\Big)^{\lambda_{(k)}}\Big]f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t), \tag{9}$$

where the sum is over all positive, odd L, with $L=\sum_{j=1}^{d} l_j+\sum_{k=1}^{N}\lambda_k$ where l_j and λ_k are nonnegative integers; repeated indices are summed unless they are contained in parentheses, and the coefficients, J, are given by

$$J(\mathbf{x},\xi_i,l_i,\lambda_i)=\Big[\prod_{j=1}^{d}\frac{1}{l_{(j)}!}\Big(\frac{\partial}{\partial x_{(j)}}\Big)^{l_{(j)}}\Big]\Big[\prod_{k=1}^{N}\frac{1}{\lambda_{(k)}!}\Big(\frac{\partial}{\partial \xi_{(k)}}\Big)^{\lambda_{(k)}}\Big]V(\mathbf{x},\xi_i). \tag{10}$$

The initial condition is

$$f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t_0)=$$
$$\frac{f_{sur}(\xi_i,\sigma_i)}{(\pi\hbar)^d}\exp\Big[-\frac{(\mathbf{x}-\mathbf{x}_0)^2}{2\hbar\gamma}-\frac{2\gamma(\mathbf{p}-\mathbf{p}_0)^2}{\hbar}\Big], \tag{11}$$

where

$$f_{sur}(\xi_i,\sigma_i)=\prod_{i=1}^{N}\frac{1}{\pi\hbar}\tanh\Big(\frac{\omega_{(i)}}{2k_B\tau}\Big)\exp\Big[-\tanh\Big(\frac{\omega_{(i)}}{2k_B\tau}\Big)\Big(\frac{\omega_{(i)}\xi_{(i)}^2}{\hbar}+\frac{\sigma_{(i)}^2}{\hbar\omega_{(i)}}\Big)\Big]. \tag{12}$$

The classical trajectory is defined by the equations

$$\begin{aligned}
\mathbf{p}^{cl}(t)&=m\dot{\mathbf{x}}^{cl}(t)\\
\dot{\mathbf{p}}^{cl}(t)&=-\frac{\partial V(\mathbf{x},\xi_i)}{\partial \mathbf{x}}\Big|_{\mathbf{x}=\mathbf{x}^{cl}(t);\xi_i=\xi_i^{cl}(t)}\\
\sigma_i^{cl}(t)&=\dot{\xi}_i^{cl}(t)\\
\dot{\sigma}_i^{cl}(t)&=-\omega_{(i)}^2\xi_{(i)}^{cl}(t)-\frac{\partial V(\mathbf{x},\xi_i)}{\partial \xi_i}\Big|_{\mathbf{x}=\mathbf{x}^{cl}(t);\xi_i=\xi_i^{cl}(t)},
\end{aligned} \tag{13}$$

and the initial conditions $\mathbf{x}^{cl}(t_0)=\mathbf{x}_0$, $\mathbf{p}^{cl}(t_0)=\mathbf{p}_0$, $\xi_i^{cl}(t_0)=0$, and $\sigma_i^{cl}(t_0)=0$. We assume the incidon does not stick to the surface so that $\mathbf{x}^{cl}(t)\cdot\hat{\mathbf{n}}\to\infty$ as $t\to\infty$.

Defining a distribution function, g, so that

$$g(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t)=(\hbar)^{d+N}f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t), \tag{14}$$

where

$$
\begin{aligned}
\mathbf{r} &= \frac{1}{\sqrt{\hbar}}[\mathbf{x} - \mathbf{x}^{cl}(t)] \\
\mathbf{s} &= \frac{1}{\sqrt{\hbar}}[\mathbf{p} - \mathbf{p}^{cl}(t)] \\
\epsilon_i &= \frac{1}{\sqrt{\hbar}}[\xi_i - \xi_i^{cl}(t)] \\
\varsigma_i &= \frac{1}{\sqrt{\hbar}}[\sigma_i - \sigma_i^{cl}(t)],
\end{aligned}
\tag{15}
$$

equation (9) may be rewritten

$$
\begin{aligned}
&\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial \varsigma_i} + \frac{1}{\sqrt{\hbar}}\frac{\partial V}{\partial x_i}|_{cl}\frac{\partial}{\partial s_i} + \frac{1}{\sqrt{\hbar}}\frac{\partial V}{\partial \xi_i}|_{cl}\frac{\partial}{\partial \sigma_i}\Big)g(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = \\
&\quad \frac{2}{i\hbar}\sum_L J(\mathbf{x},\xi_i,l_i,\lambda_i)\Big[\prod_{j=1}^{d}\Big(\frac{i\sqrt{\hbar}}{2}\frac{\partial}{\partial s_{(j)}}\Big)^{l_{(j)}}\Big]\Big[\prod_{k=1}^{N}\Big(\frac{i\sqrt{\hbar}}{2}\frac{\partial}{\partial \varsigma_{(k)}}\Big)^{\lambda_{(k)}}\Big]g(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t),
\end{aligned}
\tag{16}
$$

where the symbol "$|_{cl}$" indicates that a quantity is evaluated for the classical trajectory. The initial condition for g is

$$
\begin{aligned}
g(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t_0) &= \\
&\frac{g_{sur}(\epsilon_i,\varsigma_i)}{(\pi)^d}\exp\Big[-\frac{\mathbf{r}^2}{2\gamma} - 2\gamma\mathbf{s}^2\Big],
\end{aligned}
\tag{17}
$$

where

$$
g_{sur}(\epsilon_i,\varsigma_i) = \prod_{i=1}^{N}\frac{1}{\pi}\tanh\Big(\frac{\omega_{(i)}}{2k_B\tau}\Big)\exp\Big[-\tanh\Big(\frac{\omega_{(i)}}{2k_B\tau}\Big)\Big(\omega_{(i)}\epsilon_{(i)}^2 + \frac{\varsigma_{(i)}^2}{\omega_{(i)}}\Big)\Big],
\tag{18}
$$

and the coefficients, J, can be written

$$
\begin{aligned}
J(\mathbf{x},\xi_i,l_i,\lambda_i) &= \Big[\prod_{j=1}^{d}\frac{1}{l_{(j)}!}\Big(\frac{\partial}{\partial x_{(j)}}\Big)^{l_{(j)}}\Big]\Big[\prod_{k=1}^{N}\frac{1}{\lambda_{(k)}!}\Big(\frac{\partial}{\partial \xi_{(k)}}\Big)^{\lambda_{(k)}}\Big] \\
&\times\sum_{\Lambda=0}^{\infty}\Big[\prod_{m=1}^{d}\frac{1}{b_{(m)}!}\Big(\sqrt{\hbar}r_{(m)}\frac{\partial}{\partial x_{(m)}}\Big)^{b_{(m)}}\Big]\Big[\prod_{n=1}^{N}\frac{1}{\theta_{(n)}!}\Big(\sqrt{\hbar}\epsilon_{(n)}\frac{\partial}{\partial \xi_{(n)}}\Big)^{\theta_{(n)}}\Big]V(\mathbf{x},\xi_i)|_{cl},
\end{aligned}
\tag{19}
$$

where $\Lambda = \sum_{m=1}^{d} b_m + \sum_{n=1}^{N}\theta_n$, with b_m and θ_n being nonnegative integers.

From equations (16)-(19), one can show that g has an expansion

$$
g(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = \sum_{n=0}^{\infty}(\hbar)^{\frac{n}{2}}g_n(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t),
\tag{20}
$$

where g_n is independent of $\hbar$ and has the properties

$$\int d^d r d^d s D\epsilon_i D\varsigma_i g_0(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = 1$$

$$\int d^d r d^d s D\epsilon_i D\varsigma_i g_n(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = 0, \quad n \neq 0 \tag{21}$$

$$g_n(-\mathbf{r},-\mathbf{s},-\epsilon_i,-\varsigma_i,t) = (-1)^n g_n(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t).$$

The equations of motion for the g_n are found by substituting the expansion for g from equation (20) into equation (16) and collecting terms of the same order in $\hbar$. Using equations (8), (14), (15), (20), and (21), the $\hbar$-expansion for $< Q(\mathbf{p}) >$ can be shown to be

$$\begin{aligned} < Q(\mathbf{p}) > (t) = Q(\mathbf{p})|_{cl} + \hbar\Big[\frac{\partial Q(\mathbf{p})}{\partial p_j}|_{cl} \int d^d r d^d s D\epsilon_i D\varsigma_i g_1(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) s_j \\ + \frac{1}{2}\frac{\partial^2 Q(\mathbf{p})}{\partial p_j \partial p_k}|_{cl} \int d^d r d^d s D\epsilon_i D\varsigma_i g_0(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) s_j s_k\Big] + O(\hbar^2). \end{aligned} \tag{22}$$

Now consider a function, $\tilde{f}$, which satisfies

$$\begin{aligned} \Big(\frac{\partial}{\partial t} + \frac{p_i}{m}\frac{\partial}{\partial x_i} + \sigma_i \frac{\partial}{\partial \xi_i} - \omega_i^2 \xi_i \frac{\partial}{\partial \sigma_i}\Big)\tilde{f}(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t) = \\ \Big[\frac{\partial V(\mathbf{x},\xi_i)}{\partial x_i}\frac{\partial}{\partial p_i} + \frac{\partial V(\mathbf{x},\xi_i)}{\partial \xi_i}\frac{\partial}{\partial \sigma_i}\Big]\tilde{f}(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t), \end{aligned} \tag{23}$$

with the initial condition $\tilde{f}(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t_0) = f(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t_0)$. Equation (23) is the classical transport equation for a phase space probability distribution corresponding to the Hamiltonian H and is identical to equation (9) except that the terms with $L \neq 1$ do not appear.

The function $\tilde{g}$, defined

$$\tilde{g}(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = (\hbar)^{d+N}\tilde{f}(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t), \tag{24}$$

satisfies an equation identical to equation (16) but without the $L \neq 1$ terms and has an $\hbar$-expansion

$$\tilde{g}(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t) = \sum_{n=0}^{\infty}(\hbar)^{\frac{n}{2}}\tilde{g}_n(\mathbf{r},\mathbf{s},\epsilon_i,\varsigma_i,t). \tag{25}$$

$\tilde{g}$ also has the properties given in equation (21).

The equations of motion for g_0 and $\tilde{g}_0$ are identical, and hence $g_0 = \tilde{g}_0$ for all times. Although the equations for g_1 and $\tilde{g}_1$ are different, it can be shown (see Appendix A) that

$$\int d^d r d^d s D\epsilon_i D\varsigma_i \tilde{g}_1(\mathbf{r}, \mathbf{s}, \epsilon_i, \varsigma_i, t) s_j = \int d^d r d^d s D\epsilon_i D\varsigma_i g_1(\mathbf{r}, \mathbf{s}, \epsilon_i, \varsigma_i, t) s_j. \tag{26}$$

From equation (22), we then have

$$\begin{aligned} < Q(\mathbf{p}) > (t) =& Q(\mathbf{p})|_{cl} + \hbar\Big[\frac{\partial Q(\mathbf{p})}{\partial p_j}|_{cl} \int d^d r d^d s D\epsilon_i D\varsigma_i \tilde{g}_1(\mathbf{r}, \mathbf{s}, \epsilon_i, \varsigma_i, t) s_j \\ &+ \frac{1}{2}\frac{\partial^2 Q(\mathbf{p})}{\partial p_j \partial p_k}|_{cl} \int d^d r d^d s D\epsilon_i D\varsigma_i \tilde{g}_0(\mathbf{r}, \mathbf{s}, \epsilon_i, \varsigma_i, t) s_j s_k\Big] + O(\hbar^2) \\ =& \int d^d x d^d p D\xi_i D\sigma_i Q(\mathbf{p}) \tilde{f}(\mathbf{x}, \mathbf{p}, \xi_i, \sigma_i, t) + O(\hbar^2). \end{aligned} \tag{27}$$

Therefore, the classical phase space distribution, $\tilde{f}$, gives the correct quantum expectation value for Q up to order $\hbar$.

We define a set of classical trajectories by

$$\begin{aligned} \mathbf{p}^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& m\dot{\mathbf{x}}^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') \\ \dot{\mathbf{p}}^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& -\frac{\partial V(\mathbf{x}, \xi_i)}{\partial \mathbf{x}}|_{tr} \\ \sigma_i^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& \dot{\xi}_i^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') \\ \dot{\sigma}_i^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& -\omega_{(i)}^2 \xi_{(i)}^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') - \frac{\partial V(\mathbf{x}, \xi_i)}{\partial \xi_i}|_{tr}, \end{aligned} \tag{28}$$

where the derivatives of $V(\mathbf{x}, \xi_i)$ are evaluated at

$$\begin{aligned} \mathbf{x} =& \mathbf{x}^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') \\ \xi_i =& \xi_i^{tr}(t, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i'), \end{aligned} \tag{29}$$

and with the initial conditions

$$\begin{aligned} \mathbf{x}^{tr}(t_0, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& \mathbf{x}' \\ \mathbf{p}^{tr}(t_0, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& \mathbf{p}' \\ \xi_i^{tr}(t_0, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& \xi_i' \\ \sigma_i^{tr}(t_0, \mathbf{x}', \mathbf{p}', \xi_i', \sigma_i') =& \sigma_i'. \end{aligned} \tag{30}$$

The solution to equation (23) can then be written

$$\tilde{f}(\mathbf{x},\mathbf{p},\xi_i,\sigma_i,t) = \int d^dx'd^dp'D\xi_i'D\sigma_i'\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0) \times \delta^d[\mathbf{x}-\mathbf{x}^{tr}(t,\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i')]\delta^d[\mathbf{p}-\mathbf{p}^{tr}(t,\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i')] \times \prod_{i=1}^{N}\left\{\delta[\xi_i-\xi_i^{tr}(t,\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i')]\delta[\sigma_i-\sigma_i^{tr}(t,\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i')]\right\}, \quad (31)$$

which implies

$$< Q(\mathbf{p}) > (t) = \int d^dx'd^dp'D\xi_i'D\sigma_i'Q[\mathbf{p}^{tr}(t,\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i')]\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0) + O(\hbar^2). \quad (32)$$

Expanding about the initial values for the classical trajectory of equation (13) yields

$$< Q(\mathbf{p}) > (t) = Q[\mathbf{p}^{cl}(t)] + \frac{1}{2}\frac{\partial^2 Q}{\partial x_i'^2}|_{cl}\delta^2 x_i' + \frac{1}{2}\frac{\partial^2 Q}{\partial p_i'^2}|_{cl}\delta^2 p_i' + \frac{1}{2}\frac{\partial^2 Q}{\partial \xi_i'^2}|_{cl}\delta^2 \xi_i' + \frac{1}{2}\frac{\partial^2 Q}{\partial \sigma_i'^2}|_{cl}\delta^2 \sigma_i' + O(\hbar^2), \quad (33)$$

where

$$\begin{aligned}
\frac{\partial^2 Q}{\partial x_i'^2}|_{cl} &= \frac{\partial^2 Q[\mathbf{p}^{tr}(t,\mathbf{x}',\mathbf{p}_0,0,0)]}{\partial x_i'^2}|_{\mathbf{x}'=\mathbf{x}_0} \\
\frac{\partial^2 Q}{\partial p_i'^2}|_{cl} &= \frac{\partial^2 Q[\mathbf{p}^{tr}(t,\mathbf{x}_0,\mathbf{p}',0,0)]}{\partial p_i'^2}|_{\mathbf{p}'=\mathbf{p}_0} \\
\frac{\partial^2 Q}{\partial \xi_i'^2}|_{cl} &= \frac{\partial^2 Q[\mathbf{p}^{tr}(t,\mathbf{x}_0,\mathbf{p}_0,\xi_i',0)]}{\partial \xi_i'^2}|_{\xi_i'=0} \\
\frac{\partial^2 Q}{\partial \sigma_i'^2}|_{cl} &= \frac{\partial^2 Q[\mathbf{p}^{tr}(t,\mathbf{x}_0,\mathbf{p}_0,0,\sigma_i')]}{\partial \sigma_i'^2}|_{\sigma_i'=0},
\end{aligned} \quad (34)$$

and

$$\begin{aligned}
\delta^2 x_i' &= \int d^dx'd^dp'D\xi_i'D\sigma_i'\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0)[x_i'-(\mathbf{x}_0)_i]^2 = \hbar\gamma \\
\delta^2 p_i' &= \int d^dx'd^dp'D\xi_i'D\sigma_i'\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0)[p_i'-(\mathbf{p}_0)_i]^2 = \frac{\hbar}{4\gamma} \\
\delta^2 \xi_i' &= \int d^dx'd^dp'D\xi_i'D\sigma_i'\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0)\xi_i'^2 = \frac{\hbar}{2\omega_i}\coth\frac{\omega_i}{2k_B\tau} \\
\delta^2 \sigma_i' &= \int d^dx'd^dp'D\xi_i'D\sigma_i'\tilde{f}(\mathbf{x}',\mathbf{p}',\xi_i',\sigma_i',t_0)\sigma_i'^2 = \frac{\hbar\omega_i}{2}\coth\frac{\omega_i}{2k_B\tau}.
\end{aligned} \quad (35)$$

In order to obtain the semiclassical shift, ΔQ, we must average equation (33) over the impact parameter, differentiate with respect to $\hbar$, and take the limits indicated by equation

(6). Doing this causes the first three terms on the right side of equation (33) to vanish, as well as those of order $\hbar^2$ or higher. The first term vanishes since it is independent of $\hbar$, and the third term vanishes since $\delta^2 p_i'$ goes to zero as γ tends to infinity. The components of the second term perpendicular to $\hat{\mathbf{n}}$ vanish upon averaging over the impact parameter, while the component parallel to $\hat{\mathbf{n}}$ vanishes since the final momentum of the incidon becomes independent of $\mathbf{x}_0 \cdot \hat{\mathbf{n}}$ as $(t - t_0) \to \infty$ and $\mathbf{x}_0 \cdot \hat{\mathbf{n}} \to \infty$. Thus, the semiclassical shift is given by

$$\Delta Q = \frac{1}{2}\frac{\partial^2 Q_a}{\partial \xi_i'^2}|_{fc}\delta^2 \xi_i' + \frac{1}{2}\frac{\partial^2 Q_a}{\partial \sigma_i'^2}|_{fc}\delta^2 \sigma_i', \tag{36}$$

where

$$\begin{aligned} \frac{\partial^2 Q_a}{\partial \xi_i'^2}|_{fc} &= \lim_{\mathbf{x}_0\cdot\hat{\mathbf{n}}\to\infty}\left(\lim_{(t-t_0)\to\infty}\left(\frac{\partial^2 Q}{\partial \xi_i'^2}|_{cl}\right)_a\right) \\ \frac{\partial^2 Q_a}{\partial \sigma_i'^2}|_{fc} &= \lim_{\mathbf{x}_0\cdot\hat{\mathbf{n}}\to\infty}\left(\lim_{(t-t_0)\to\infty}\left(\frac{\partial^2 Q}{\partial \sigma_i'^2}|_{cl}\right)_a\right), \end{aligned} \tag{37}$$

with the subscript a indicating the average over the impact parameter and the subscript fc indicating a quantity evaluated for the final, classical scattered state after the limits $\mathbf{x}_0 \cdot \hat{\mathbf{n}} \to \infty$ and $(t - t_0) \to \infty$ have been taken.

Equation (36) may be rewritten in terms of coordinates, y_i, which represent the displacements of the surface atoms from their equilibrium positions, as

$$\Delta Q = \frac{1}{2}\frac{\partial^2 Q_a}{\partial y_i' \partial y_j'}|_{fc} < y_i y_j >_0 + \frac{1}{2}\frac{\partial^2 Q_a}{\partial \dot{y}_i' \partial \dot{y}_j'}|_{fc} < \dot{y}_i \dot{y}_j >_0, \tag{38}$$

where the correlations for the surface atom coordinates are evaluated in thermal equilibrium. Equation (38) has a simple physical interpretation. Consider the classical scattering of an incidon off a surface where the surface atom coordinates initially obey a Gaussian probability distribution with the property that it implies atom-atom correlations identical to the equilibrium quantum mechanical atom-atom correlations. Then the average value of $Q(\mathbf{p})$ for the final scattered state will be equal to the expectation value of $Q(\mathbf{p})$ for the corresponding quantum problem to order $\hbar$. Approximations using classical trajectories with quantum initial conditions have been applied to molecular scattering[11] and to the calculation of relaxation rates for particles interacting with heat baths.[12,13] Equation (38) justifies this approach for atom-surface scattering in the semiclassical limit.

We finally note that if $2k_BT \gg \hbar\omega_i$ for all ω_i, then $\Delta Q \propto T$ for any Q.

IV. One-dimensional Example with Comparison to Trajectory Approximation

As an application of the results of the previous section, we consider a one-dimensional example where the surface consists of a single harmonic oscillator. The Hamiltonian is

$$H_{1d} = \frac{p^2}{2m} + \frac{q^2}{2M} + \frac{1}{2}M\omega^2 y^2 + V_0 \exp\Big[-\frac{(x-y)}{R}\Big], \tag{39}$$

where $q = \sqrt{M}\sigma$ and $y = \xi/\sqrt{M}$ with σ and ξ being the oscillator's normal coordinates, and M is the oscillator's mass. Equation (38) gives

$$\Delta p = \frac{1}{2}\frac{\partial^2 p}{\partial y'^2}|_{fc} < y^2 >_0 + \frac{1}{2}\frac{\partial^2 p}{\partial \dot{y}'^2}|_{fc} < \dot{y}^2 >_0, \tag{40}$$

and

$$\delta^2 p = \Big(\frac{\partial p}{\partial y'}|_{fc}\Big)^2 < y^2 >_0 + \Big(\frac{\partial p}{\partial \dot{y}'}|_{fc}\Big)^2 < \dot{y}^2 >_0, \tag{41}$$

where $\delta^2 p =< (p - p^{cl})^2 >_f + O(\hbar^2)$ is the momentum uncertainty of the final incidon state. Equation (38) also implies

$$\Delta Q = \frac{dQ(p)}{dp}|_{fc}\Delta p + \frac{1}{2}\frac{d^2Q(p)}{dp^2}|_{fc}\delta^2 p \tag{42}$$

and

$$\delta^2 Q = \Big(\frac{dQ(p)}{dp}|_{fc}\Big)^2 \delta^2 p, \tag{43}$$

where $\delta^2 Q =< [Q(p) - Q_{cl}]^2 >_f + O(\hbar^2)$. Equations (42) and (43) imply that the semiclassical shift and uncertainty for any quantity may be found from the shift and uncertainty for p and the final value of p^{cl}.

The trajectory approximation has been developed to calculate the final energy distribution of the incidon (and for a flat surface the momentum distribution as well). Although predictions based on the trajectory approximation have been compared to experiment with some apparent success,[5-8] a compelling theoretical justification for it has not been given. To test its validity, we compare the semiclassical momentum shift and uncertainty predicted by the trajectory approximation to the exact results calculated from equations (40) and (41).

The essence of the trajectory approximation is that the incidon is assumed to follow the classical trajectory, while the surface atoms are treated quantum mechanically with a time-dependent interaction potential, $V[\mathbf{x}^{cl}(t), \xi_i]$. The final energy distribution, $P_s(E)$, for the surface is then calculated, and the final energy distribution for the incidon is inferred from the relationship

$$P_{ind}(E) = \int dE' P_s'(E') P_s(E_0 + E' - E), \tag{44}$$

which follows from energy conservation, where $P_s'(E')$ is the initial energy distribution for the surface and E_0 is the initial incidon energy.

Using arguments similar to those of section III, we can obtain expressions for the semiclassical limit of the final energy shift and energy width in the trajectory approximation. For simplicity, we confine ourselves to the particular system described by H_{1d}. We define a set of trajectories by

$$M\ddot{y}^{ta}(t,y',\dot{y}') = -\omega^2 y^{ta}(t,y',\dot{y}') - \frac{V_0}{R}\exp\Big[\frac{y^{ta}(t,y',\dot{y}') - x^{cl}(t)}{R}\Big], \tag{45}$$

with the initial conditions

$$\begin{aligned} y^{ta}(t_0,y',\dot{y}') &= y' \\ \dot{y}^{ta}(t_0,y',\dot{y}') &= \dot{y}', \end{aligned} \tag{46}$$

and an energy by

$$E_S^{ta}(y',\dot{y}') = \frac{M}{2}\Big([y^{ta}(t,y',\dot{y}')]^2 + \omega^2[\dot{y}^{ta}(t,y',\dot{y}')]^2\Big). \tag{47}$$

The semiclassical energy shift and uncertainty for the surface in the trajectory approximation are then

$$\Delta E_S^{ta} = \frac{1}{2}\frac{\partial^2 E_S^{ta}}{\partial y'^2}|_{fc} < y^2 >_0 + \frac{1}{2}\frac{\partial^2 E_S^{ta}}{\partial \dot{y}'^2}|_{fc} < \dot{y}^2 >_0, \tag{48}$$

and

$$\delta^2 E_S^{ta} = \Big(\frac{\partial E_S^{ta}}{\partial y'}|_{fc}\Big)^2 < y^2 >_0 + \Big(\frac{\partial E_S^{ta}}{\partial \dot{y}'}|_{fc}\Big)^2 < \dot{y}^2 >_0 . \tag{49}$$

From energy conservation, the energy shift, ΔE_{ind}^{ta}, and energy uncertainty, $\delta^2 E_{ind}^{ta}$, for the incidon are inferred to be

$$\begin{aligned} \Delta E_{ind}^{ta} &= \overline{E}'_S - \Delta E_S^{ta} \\ \delta^2 E_{ind}^{ta} &= \delta^2 E_S^{ta}, \end{aligned} \tag{50}$$

where $\overline{E}'_S$ is the initial mean energy of the surface. Using equations (42) and (43), the momentum shift and uncertainty for the incidon may be written as

$$\begin{aligned} \Delta p^{ta} &= \frac{m}{p_{fc}}\Delta E_{ind}^{ta} - \frac{m^2}{2p_{fc}^3}\delta^2 E_{ind}^{ta} \\ \delta^2 p^{ta} &= \frac{m^2}{p_{fc}^2}\delta^2 E_{ind}^{ta}, \end{aligned} \tag{51}$$

where p_{fc} is the final value of the incidon's classical momentum.

Without loss of generality, we may choose units so that $M = \omega = 1$ and so $p_0/m = -1$. We may also set $V_0 = 1$, since a change in V_0 is equivalent to a shift in the coordinate x. Assuming the surface oscillator is initially at zero temperature, the system then has, excluding $\hbar$, two independent parameters which we take as $\varsigma = 1/R$ and $\eta = m/R$.

In Figures 1-3, the exact momentum shift and that predicted by the trajectory approximation are plotted as a function of η for ς equal to 1, 2, and 5, and similarly Figures 4-6 show the momentum uncertainty versus η. The ratio of the momentum uncertainty in trajectory approximation to the exact value is plotted in Figure 7.

We see from the figures that in general the predictions of trajectory approximation deviate significantly from the exact result for both the shift and the uncertainty. However, when either η or ς is small the trajectory approximation accurately predicts the momentum uncertainty (but not the shift). In Appendix B, we prove that the trajectory approximation becomes exact fo: :he uncertainty either if $\eta \ll 1$ or if $\varsigma \ll 1$ and that $\eta \ll 1$ corresponds to the maximum deflection of the oscillator being small compared to the interaction range, R, while $\varsigma \ll 1$ corresponds to the interaction between the incidon and the oscillator being adiabatic. We also note, without giving a proof, that both the exact and trajectory approximation values for the shift and uncertainty have zeros whenever the classical collision is perfectly elastic.

V. Conclusions

Our main result of equation (38) provides a simple method for obtaining the semiclassical limit of functions of the incidon's final momentum. It requires only the equilibrium correlations of the surface atoms and quantities derivable from classical trajectories to be calculated. We expect this method to be useful for physically interesting surfaces.

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Appendix A

In this appendix we justify equation (26). Defining the $(d+N)$-dimensional vectors

$$\begin{aligned} A_\mu &= (\mathbf{x}, \xi_i) \\ B_\mu &= (\mathbf{r}, \epsilon_i) \qquad (A1) \\ C_\mu &= (\mathbf{s}, \varsigma_i), \end{aligned}$$

equation (16) can be rewritten

$$\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial\varsigma_i} + \frac{1}{\sqrt{\hbar}}\frac{\partial V}{\partial A_\mu}|_{cl}\frac{\partial}{\partial C_\mu}\Big)g(B_\mu, C_\mu, t) = \frac{2}{i\hbar}\sum_G J'(A_\mu, l_\mu)\Big[\prod_{\mu=1}^{d+N}\Big(\frac{i\sqrt{\hbar}}{2}\frac{\partial}{\partial C_{(\mu)}}\Big)^{l_{(\mu)}}\Big]g(B_\mu, C_\mu, t), \tag{A2}$$

where the sum is over all positive, odd G, with $G = \sum_{\mu=1}^{d+N} l_\mu$ where l_μ is a nonnegative integer; the coefficients J' are given by

$$J'(A_\mu, l_\mu) = \Big[\prod_{\mu=1}^{d+N}\frac{1}{l_{(\mu)}!}\Big(\frac{\partial}{\partial A_{(\mu)}}\Big)^{l_{(\mu)}}\Big]\sum_{\Gamma=0}^{\infty}\Big[\prod_{\nu=1}^{d}\frac{1}{b_{(\nu)}!}\Big(\sqrt{\hbar}B_{(\nu)}\frac{\partial}{\partial A_{(\nu)}}\Big)^{b_{(\nu)}}\Big]V(A_\mu)|_{cl}, \tag{A3}$$

where $\Gamma = \sum_{\nu=1}^{d+N} b_\nu$ with b_ν being a nonnegative integer.

Using the expansion from equation (20), we obtain

$$\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial\varsigma_i}\Big)g_0(B_\mu, C_\mu, t) = \frac{\partial^2 V(A_\mu)}{\partial A_\mu \partial A_\nu}|_{cl}B_\nu\frac{\partial}{\partial C_\mu}g_0(B_\mu, C_\mu, t), \tag{A4}$$

and

$$\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial\varsigma_i}\Big)g_1(B_\mu, C_\mu, t) = \frac{\partial^2 V(A_\mu)}{\partial A_\mu \partial A_\nu}|_{cl}B_\nu\frac{\partial}{\partial C_\mu}g_1(B_\mu, C_\mu, t) + \frac{1}{2}\frac{\partial^3 V(A_\mu)}{\partial A_\mu\partial A_\nu\partial A_\kappa}|_{cl}B_\nu B_\kappa\frac{\partial}{\partial C_\mu}g_0(B_\mu, C_\mu, t) - \frac{1}{24}\frac{\partial^3 V(A_\mu)}{\partial A_\mu\partial A_\nu\partial A_\kappa}|_{cl}\frac{\partial^3 g_0(B_\mu, C_\mu, t)}{\partial C_\mu\partial C_\nu\partial C_\kappa}. \tag{A5}$$

The equation for $\tilde{g}_0$ is identical to that for g_0, and since g and $\tilde{g}$ have the same initial conditions, we have $\tilde{g}_0 = g_0$. The equation for $\tilde{g}_1$ is

$$\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial\varsigma_i}\Big)\tilde{g}_1(B_\mu, C_\mu, t) = \frac{\partial^2 V(A_\mu)}{\partial A_\mu \partial A_\nu}|_{cl}B_\nu\frac{\partial}{\partial C_\mu}\tilde{g}_1(B_\mu, C_\mu, t) + \frac{1}{2}\frac{\partial^3 V(A_\mu)}{\partial A_\mu\partial A_\nu\partial A_\kappa}|_{cl}B_\nu B_\kappa\frac{\partial}{\partial C_\mu}\tilde{g}_0(B_\mu, C_\mu, t). \tag{A6}$$

Subtracting equation (A6) from (A5), we find

$$\Big(\frac{\partial}{\partial t} + \frac{s_i}{m}\frac{\partial}{\partial r_i} + \varsigma_i\frac{\partial}{\partial \epsilon_i} - \omega_i^2\epsilon_i\frac{\partial}{\partial\varsigma_i}\Big)\Delta g_1(B_\mu, C_\mu, t) = \frac{\partial^2 V(A_\mu)}{\partial A_\mu \partial A_\nu}|_{cl}B_\nu\frac{\partial}{\partial C_\mu}\Delta g_1(B_\mu, C_\mu, t) - \frac{1}{24}\frac{\partial^3 V(A_\mu)}{\partial A_\mu\partial A_\nu\partial A_\kappa}|_{cl}\frac{\partial^3 g_0(B_\mu, C_\mu, t)}{\partial C_\mu\partial C_\nu\partial C_\kappa}, \tag{A7}$$

where $\Delta g_1 = g_1 - \tilde{g}_1$. Defining

$$\begin{aligned} \Delta r_j(t) &= \int DB_\mu DC_\mu \Delta g_1(B_\mu, C_\mu, t) r_j \\ \Delta s_j(t) &= \int DB_\mu DC_\mu \Delta g_1(B_\mu, C_\mu, t) s_j, \end{aligned} \tag{A8}$$

equation (A7) may be used to show

$$\begin{aligned} \Delta s_j(t) =& m \Delta \dot{r}_j(t) \\ \Delta \dot{s}_j(t) =& - \frac{\partial^2 V(A_\mu)}{\partial A_j \partial A_k}|_{cl} \Delta r_k(t), \end{aligned} \tag{A9}$$

assuming that $g(B_\mu, C_\mu)$ and its derivatives go to zero as any of its arguments goes to infinity. Since initially $\Delta r_j(t_0) = \Delta s_j(t_0) = 0$, the unique solution to (A9) is $\Delta r_j(t) = \Delta s_j(t) = 0$ which suffices to demonstrate equation (26).

Appendix B

Here we show that the trajectory approximation predicts the correct momentum uncertainty for either $\eta \ll 1$ or $\varsigma \ll 1$. We use units with $M = \omega = -p_0/m = 1$ and set $V_0 = 1$.

Defining a set of classical trajectories by

$$\begin{aligned} \eta \ddot{x}^{tr}(t, y', \dot{y}') =& \varsigma^2 e^{\varsigma[y^{tr}(t,y',\dot{y}') - x^{tr}(y',\dot{y}',t)]} \\ \ddot{y}^{tr}(t, y', \dot{y}') =& - y^{tr}(t, y', \dot{y}') - \varsigma e^{\varsigma[y^{tr}(t,y',\dot{y}') - x^{tr}(t,y',\dot{y}')]}, \end{aligned} \tag{B1}$$

with the initial condtions

$$\begin{aligned} x^{tr}(t_0, y', \dot{y}') =& x_0 \\ \dot{x}^{tr}(t_0, y', \dot{y}') =& -1 \\ y^{tr}(t_0, y', \dot{y}') =& y' \\ \dot{y}^{tr}(t_0, y', \dot{y}') =& \dot{y}', \end{aligned} \tag{B2}$$

and an energy by

$$E_S(t, y', \dot{y}') = \frac{1}{2}\Big([y^{tr}(t, y', \dot{y}')]^2 + [\dot{y}^{tr}(t, y', \dot{y}')]^2\Big), \tag{B3}$$

we have for the exact semiclassical energy uncertainty of the oscillator

$$\delta^2 E_S = \left(\frac{\partial E_S}{\partial y'}|_{fc}\right)^2 < y^2 >_0 + \left(\frac{\partial E_S}{\partial \dot{y}'}|_{fc}\right)^2 < \dot{y}^2 >_0 . \tag{B4}$$

Using $< y^2 >_0 = < \dot{y}^2 >_0 = \hbar/2$, equation (B4) may be rewritten

$$\begin{aligned}\delta^2 E_S = \frac{\hbar}{2}\Big\{ &\Big[\left(\frac{\partial y^{tr}}{\partial y'}|_{fc}\right)^2 + \left(\frac{\partial y^{tr}}{\partial \dot{y}'}|_{fc}\right)^2\Big] y_{fc}^2 + \Big[\left(\frac{\partial \dot{y}^{tr}}{\partial y'}|_{fc}\right)^2 + \left(\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{fc}\right)^2\Big] \dot{y}_{fc}^2 \\ &+ 2\Big[\frac{\partial y^{tr}}{\partial y'}|_{fc}\frac{\partial \dot{y}^{tr}}{\partial y'}|_{fc} + \frac{\partial y^{tr}}{\partial \dot{y}'}|_{fc}\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{fc}\Big] y_{fc}\dot{y}_{fc}\Big\}.\end{aligned} \tag{B5}$$

From equation (49), an expression for $\delta^2 E_S^{ta}$ can be derived which is identical to (B5) except that y^{tr} is replaced by y^{ta}, while from equation (43) and energy conservation follow

$$\frac{\delta^2 p^{ta}}{\delta^2 p} = \frac{\delta^2 E_S^{ta}}{\delta^2 E_S}. \tag{B6}$$

We first consider the case with $\eta \ll 1$. We may rewrite the second equation of (B1) as the integral equation

$$y^{tr}(t) = y' \cos(t - t_0) + \dot{y}' \sin(t - t_0) - \varsigma \int_{t_0}^{t} dt' \sin(t - t') e^{\varsigma[y^{tr}(t') - x^{tr}(t')]}, \tag{B7}$$

which, using the first equation of (B1), can also be written

$$y^{tr}(t) = y' \cos(t - t_0) + \dot{y}' \sin(t - t_0) - \frac{\eta}{\varsigma} \int_{t_0}^{t} dt' \sin(t - t') \ddot{x}^{tr}(t'). \tag{B8}$$

Taking y' and $\dot{y}'$ to be infinitesimals, we then have

$$|\varsigma y^{tr}(t)| \le \eta \int_{t_0}^{t} dt' \ddot{x}^{tr}(t') = \eta[\dot{x}^{tr}(t) - \dot{x}^{tr}(t_0)] \le 2\eta, \tag{B9}$$

since $|x^{tr}(t)| \le 1$. Therefore, if $\eta \ll 1$, then the deflection of the oscillator is much less than the range, $R \equiv \varsigma^{-1}$.

If $|\varsigma y^{tr}(t)| \ll 1$, equations B(1) may be approximated by

$$\begin{aligned}\eta \ddot{x}^{tr}(t, y', \dot{y}') &= \varsigma^2 e^{-\varsigma x^{tr}(t, y', \dot{y}')} \\ \ddot{y}^{tr}(t, y', \dot{y}') &= -\, y^{tr}(t, y', \dot{y}') - \varsigma e^{-\varsigma x^{tr}(t, y', \dot{y}')}.\end{aligned} \tag{B10}$$

Note that the equation for x^{tr} is independent of y^{tr}. Thus

$$x^{tr}(t, y', \dot{y}') = x^{tr}(t, 0, 0) \equiv x^{cl}(t), \tag{B11}$$

and

$$\ddot{y}^{tr}(t, y', \dot{y}') = -y^{tr}(t, y', \dot{y}') - \varsigma e^{-\zeta x^{cl}(t)}. \tag{B12}$$

Equation (B12) together with equation (45) imply that the trajectories used to calculate the exact uncertainty are the same as those used for the trajectory approximation. Using (B7), we then obtain the approximate solution

$$y^{tr}(t) = y^{ta}(t) = y' \cos(t - t_0) + \dot{y}' \sin(t - t_0) - \varsigma \int_{t_0}^{t} dt' \sin(t - t') e^{-\zeta x^{cl}(t')}. \tag{B13}$$

Therefore, from equation (B5), we have, for $\eta \ll 1$,

$$\delta^2 E_S = \delta^2 E_S^{ta} = \frac{\hbar}{2} \left| \int_{-\infty}^{+\infty} dt e^{it - \zeta x^{cl}(t)} \right|^2 = \hbar E_{trans}, \tag{B14}$$

where E_{trans} is the classical energy transferred to the oscillator. Equation (B14) together with (B6) show that the ratio of the trajectory approximation momentum uncertainty to the exact momentum uncertainty will be nearly unity if $\eta \ll 1$. It is straightforward to verify that the solution given in (B13) leads an energy shift of zero, and thus this approximation tells nothing about the ratio of the trajectory approximation shift to the exact shift.

We now treat the case with $\varsigma \ll 1$. Defining $\lambda(t) = \exp[-\varsigma x^{tr}(t)]$, the second equation of (B1) can be rewritten

$$\ddot{y}^{tr}(t) = -y^{tr}(t) - \varsigma \lambda(t) e^{\zeta y^{tr}(t)}. \tag{B15}$$

The oscillator's motion will be adiabatic if $\lambda(t)$ changes very little over one period of oscillation. Thus the adiabatic condition is

$$\left| \frac{\dot{\lambda}(t)}{\lambda(t)} \right| = |\varsigma \dot{x}^{tr}(t)| \ll 1. \tag{B16}$$

Since $|\dot{x}^{tr}(t)| \leq 1$, again considering y' and $\dot{y}'$ to be infinitesimals, condition (B16) is satisfied if $\varsigma \ll 1$.

From the general theory of adiabatic motion,[14] we obtain the invariant

$$I(E_{ad}, \lambda) = \int \frac{dadb}{2\pi} \Theta\Big[E_{ad} - \frac{1}{2}(a^2 + b^2) - \lambda e^{\zeta a}\Big], \tag{B17}$$

where

$$E_{ad} = \frac{1}{2}[y^{tr}]^2 + \frac{1}{2}[\dot{y}^{tr}]^2 + \lambda e^{\zeta y^{tr}}, \tag{B18}$$

is the adiabatic energy of the oscillator and Θ is a step function. In particular, $I(E_{ad}, 0) = E_{ad}$. Since both before and after the collision λ is very small, the invariance of I implies that the initial and final energies of the oscillator are equal.

In general, expanding E_S to second order in y' and $\dot{y}'$ yields

$$\begin{aligned}
E_S =& \frac{1}{2}(y^{cl})^2 + \frac{1}{2}(\dot{y}^{cl})^2 \\
&+\Big(y^{cl}\frac{\partial y^{tr}}{\partial y'}|_{cl} + \dot{y}^{cl}\frac{\partial \dot{y}^{tr}}{\partial y'}|_{cl}\Big)y' + \Big(y^{cl}\frac{\partial y^{tr}}{\partial \dot{y}'}|_{cl} + \dot{y}^{cl}\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{cl}\Big)\dot{y}' \\
&+\frac{1}{2}\Big[\Big(\frac{\partial y^{tr}}{\partial y'}|_{cl}\Big)^2 + y^{cl}\frac{\partial^2 y^{tr}}{\partial y'^2}|_{cl} + \Big(\frac{\partial \dot{y}^{tr}}{\partial y'}|_{cl}\Big)^2 + \dot{y}^{cl}\frac{\partial^2 \dot{y}^{tr}}{\partial y'^2}|_{cl}\Big]y'^2 \\
&+\frac{1}{2}\Big[\Big(\frac{\partial y^{tr}}{\partial \dot{y}'}|_{cl}\Big)^2 + y^{cl}\frac{\partial^2 y^{tr}}{\partial \dot{y}'^2}|_{cl} + \Big(\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{cl}\Big)^2 + \dot{y}^{cl}\frac{\partial^2 \dot{y}^{tr}}{\partial \dot{y}'^2}|_{cl}\Big]\dot{y}'^2 \\
&+\Big[\frac{\partial y^{tr}}{\partial y'}|_{cl}\frac{\partial y^{tr}}{\partial \dot{y}'}|_{cl} + y^{cl}\frac{\partial^2 y^{tr}}{\partial y'\partial \dot{y}'}|_{cl} + \frac{\partial \dot{y}^{tr}}{\partial y'}|_{cl}\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{cl} + \dot{y}^{cl}\frac{\partial^2 \dot{y}^{tr}}{\partial y'\partial \dot{y}'}|_{cl}\Big]y'\dot{y}' \\
&+\ldots
\end{aligned} \tag{B19}$$

Since in the adiabatic limit, the initial and final oscillator energies are equal, we have for the final energy

$$E_S = \frac{1}{2}y'^2 + \frac{1}{2}\dot{y}'^2. \tag{B20}$$

Comparing equation (B19) with (B20) gives

$$\Big(\frac{\partial y^{tr}}{\partial y'}|_{fc}\Big)^2 + \Big(\frac{\partial y^{tr}}{\partial \dot{y}'}|_{fc}\Big)^2 = \Big(\frac{\partial \dot{y}^{tr}}{\partial y'}|_{fc}\Big)^2 + \Big(\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{fc}\Big)^2 = 1 \qquad (B21),$$

and

$$\frac{\partial y^{tr}}{\partial y'}|_{fc}\frac{\partial \dot{y}^{tr}}{\partial y'}|_{fc} + \frac{\partial y^{tr}}{\partial \dot{y}'}|_{fc}\frac{\partial \dot{y}^{tr}}{\partial \dot{y}'}|_{fc} = 0. \tag{B22}$$

A similar argument shows (B21) and (B22) to be valid if y^{tr} is replaced by y^{ta}. From equation (B5), we thus obtain in the adiabatic limit

$$\delta^2 E_S = \delta^2 E_S^{ta} = \frac{\hbar}{2}(y_{fc}^2 + \dot{y}_{fc}^2) = \hbar E_{trans}, \tag{B23}$$

demonstrating that the trajectory approximation gives the correct uncertainty for $\varsigma \ll 1$.

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FIGURE CAPTIONS

1) $\Delta p/\hbar$ vs. η with $\varsigma = 1$ for the one-dimensional example. The solid line is the exact value, and the dotted line is the trajectory approximation.

2) $\Delta p/\hbar$ vs. η with $\varsigma = 2$. The solid line is the exact value, and the dotted line is the trajectory approximation.

3) $\Delta p/\hbar$ vs. η with $\varsigma = 5$. The solid line is the exact value, and the dotted line is the trajectory approximation.

4) $\delta^2 p/\hbar$ vs. η with $\varsigma = 1$. The solid line is the exact value, and the dotted line is the trajectory approximation.

5) $\delta^2 p/\hbar$ vs. η with $\varsigma = 2$. The solid line is the exact value, and the dotted line is the trajectory approximation.

6) $\delta^2 p/\hbar$ vs. η with $\varsigma = 5$. The solid line is the exact value, and the dotted line is the trajectory approximation.

7) The ratio of the momentum uncertainty in the trajectory approximation to the exact momentum uncertainty vs. η. The solid line is with $\varsigma = 5$, the dashed line is with $\varsigma = 2$, and the dotted line is with $\varsigma = 1$.

Figure 1

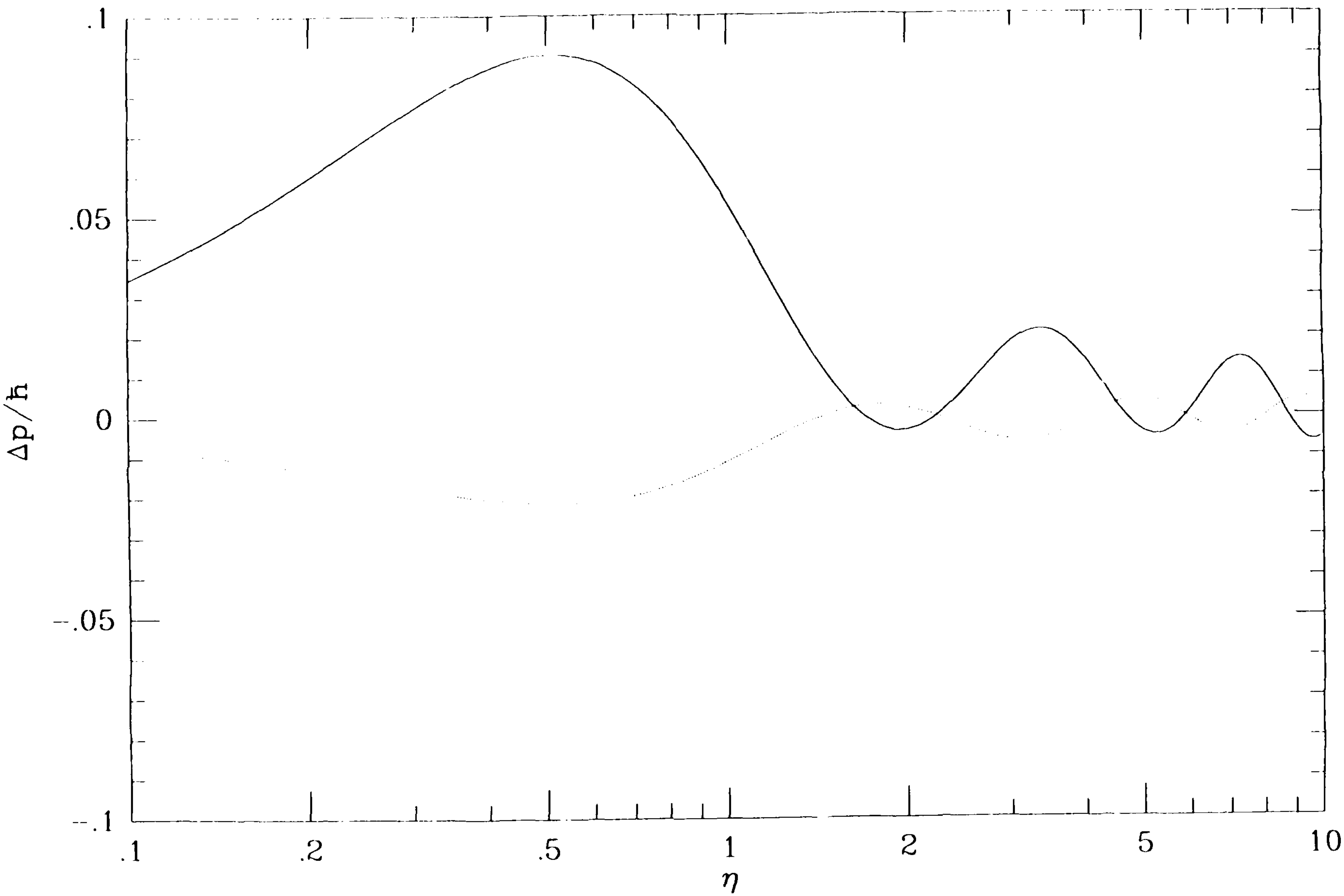


Figure 2

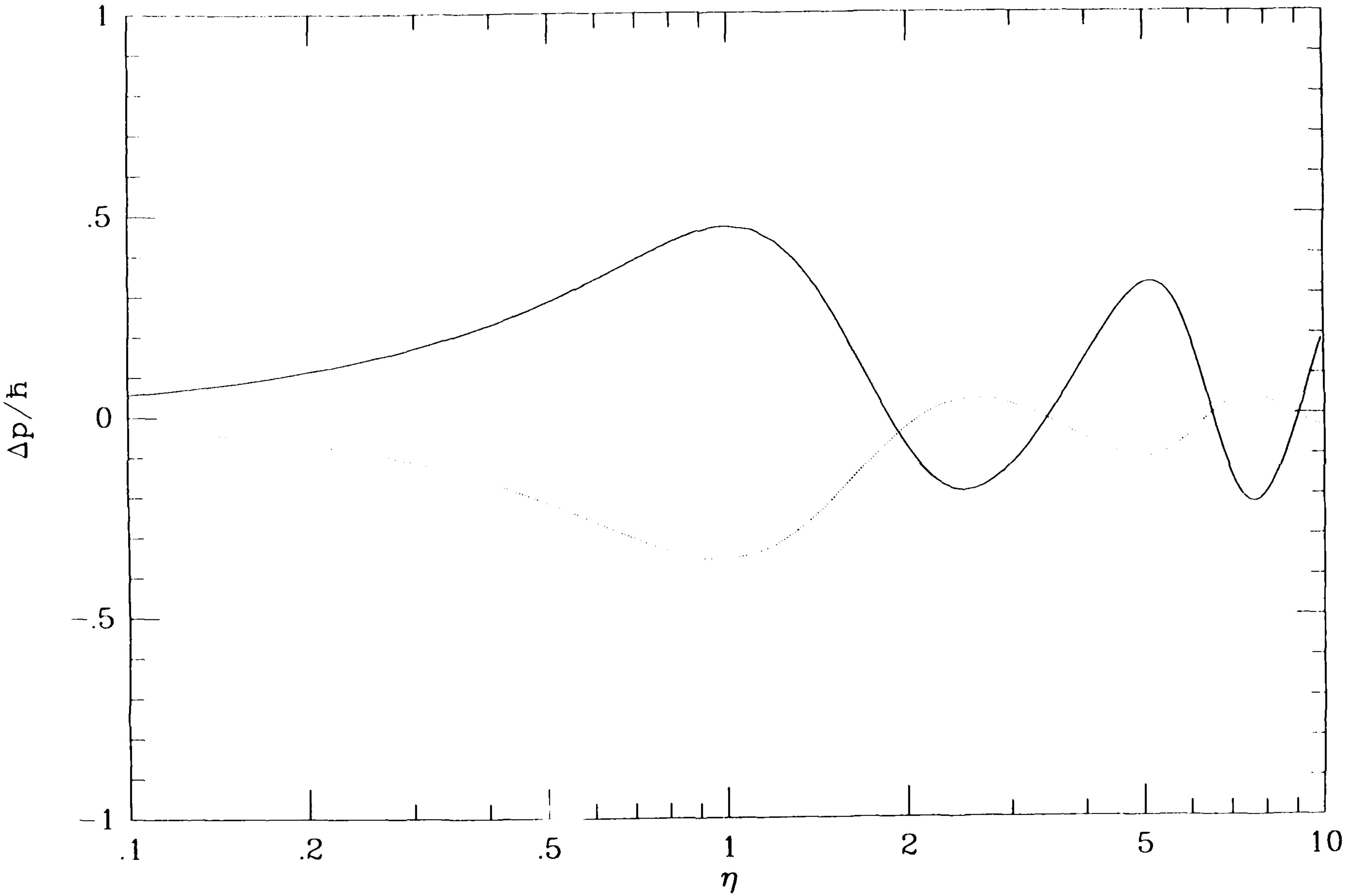


Figure 3

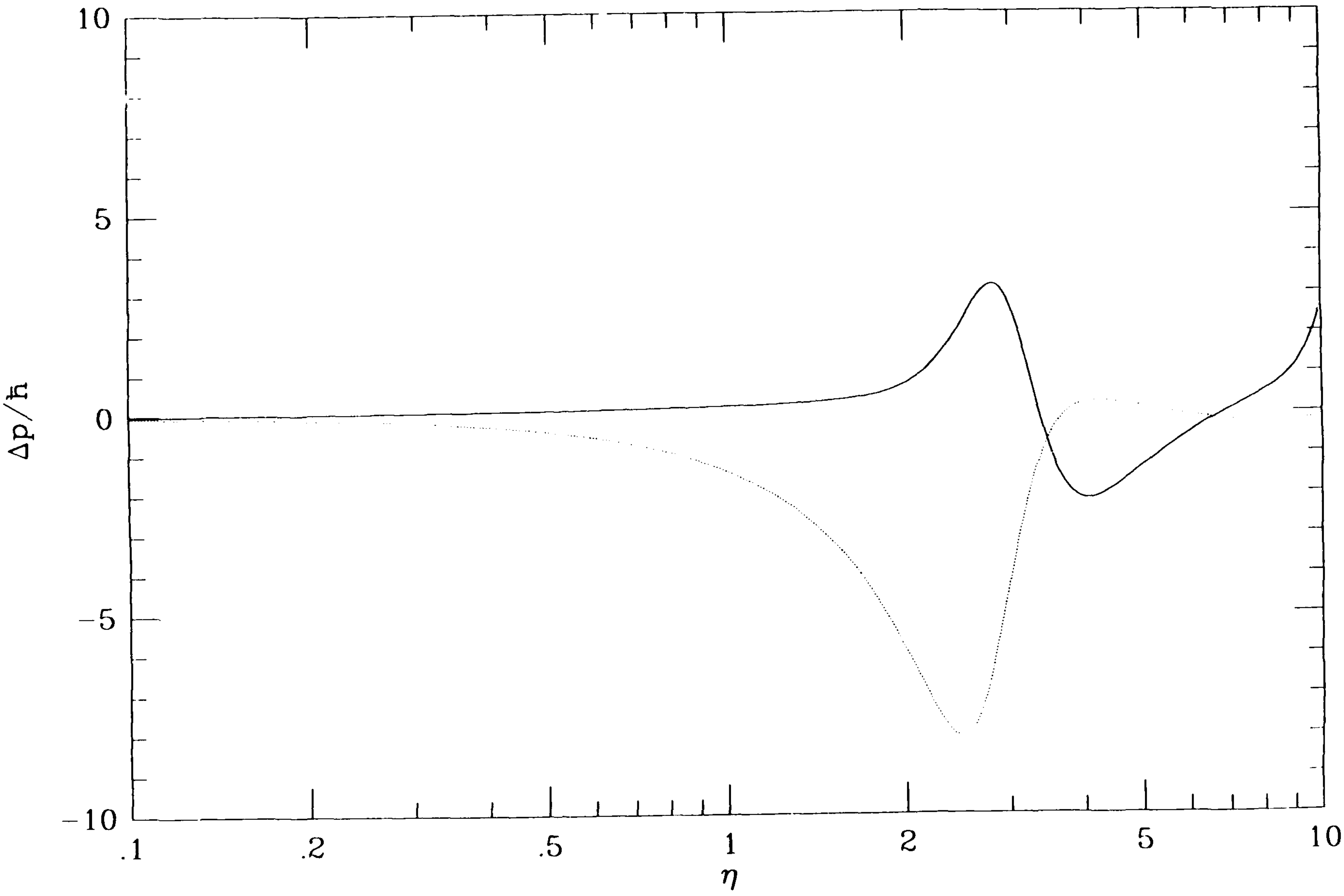


Figure 4

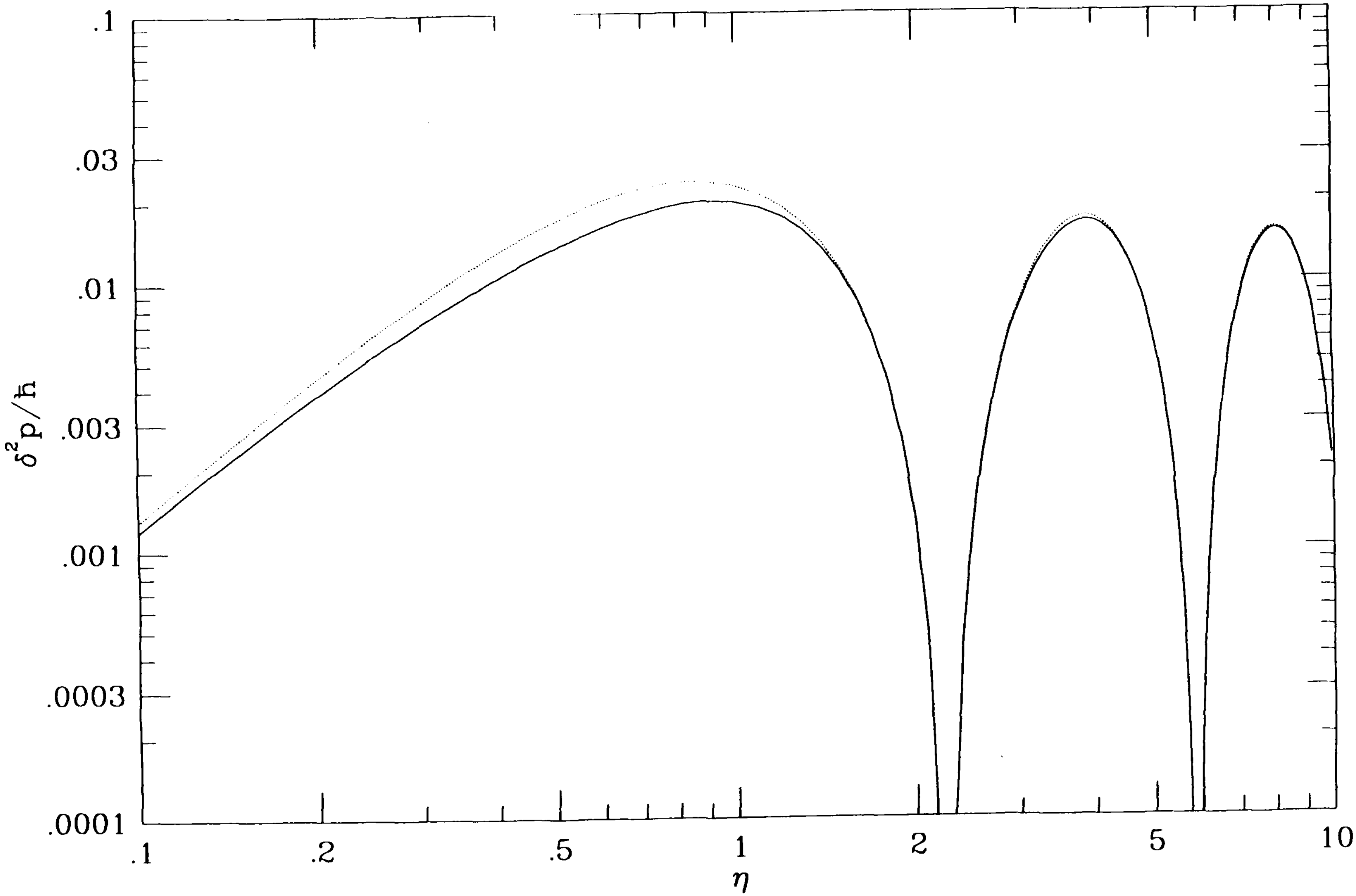


Figure 5

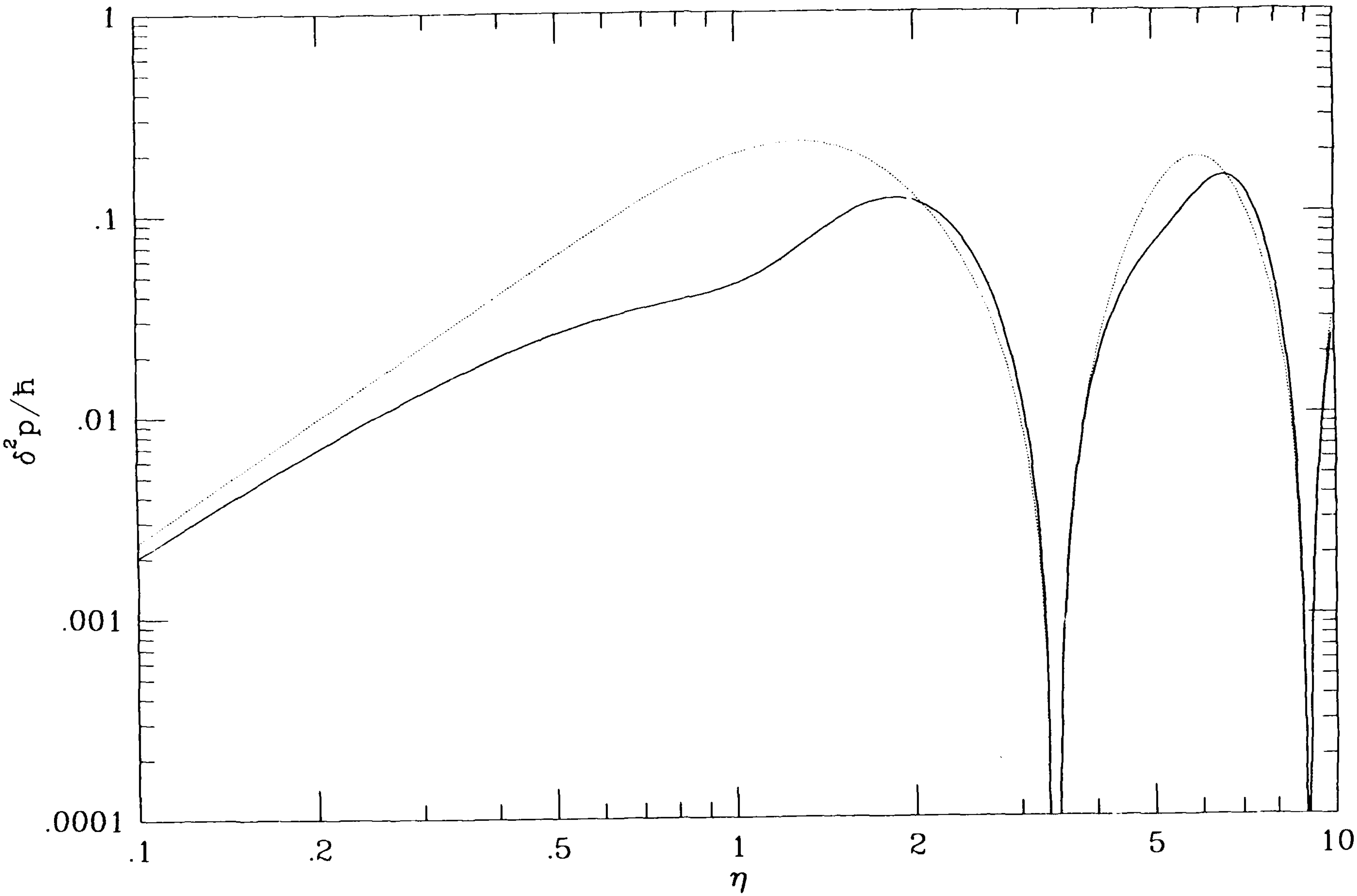


Figure 6

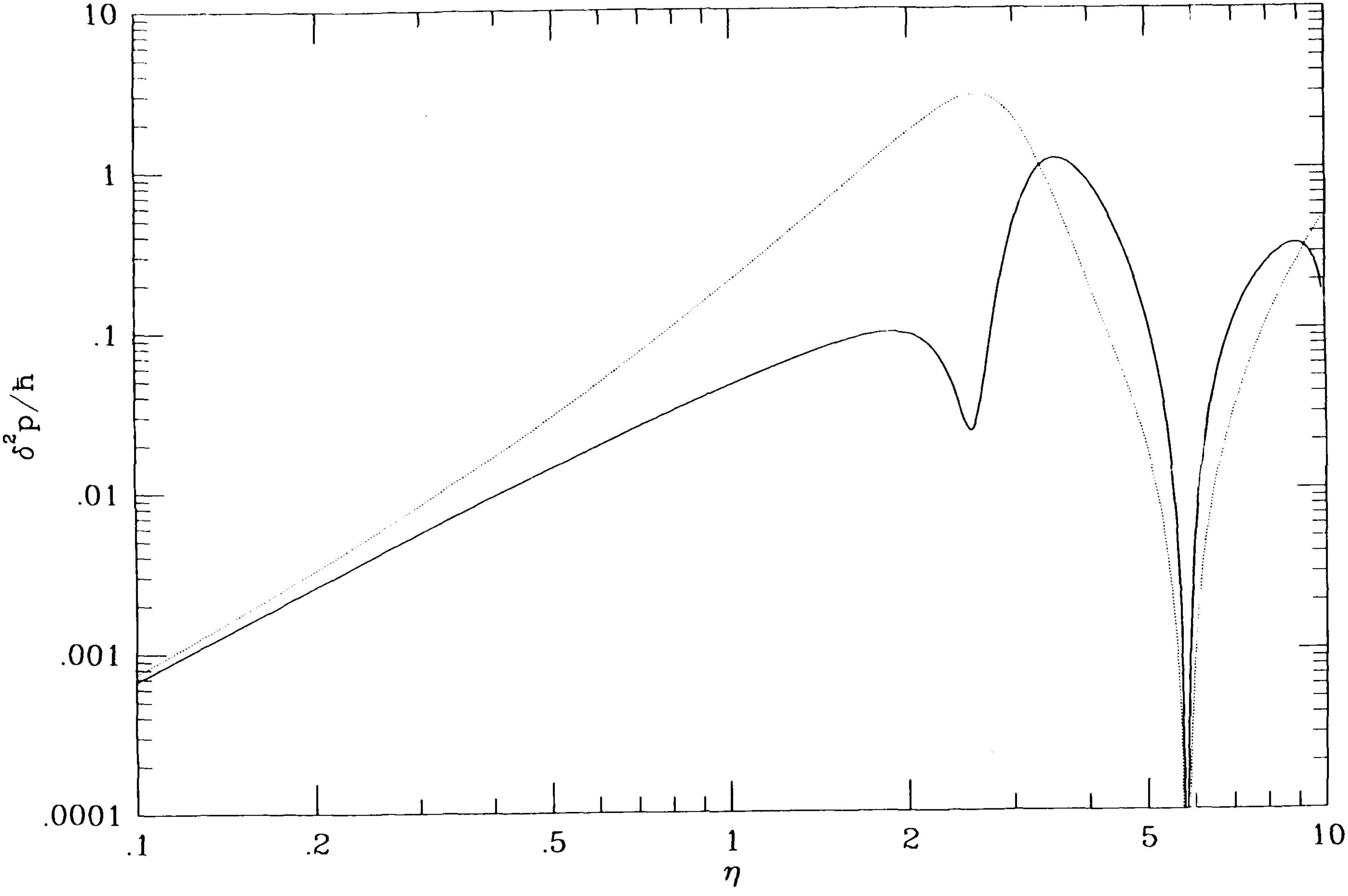
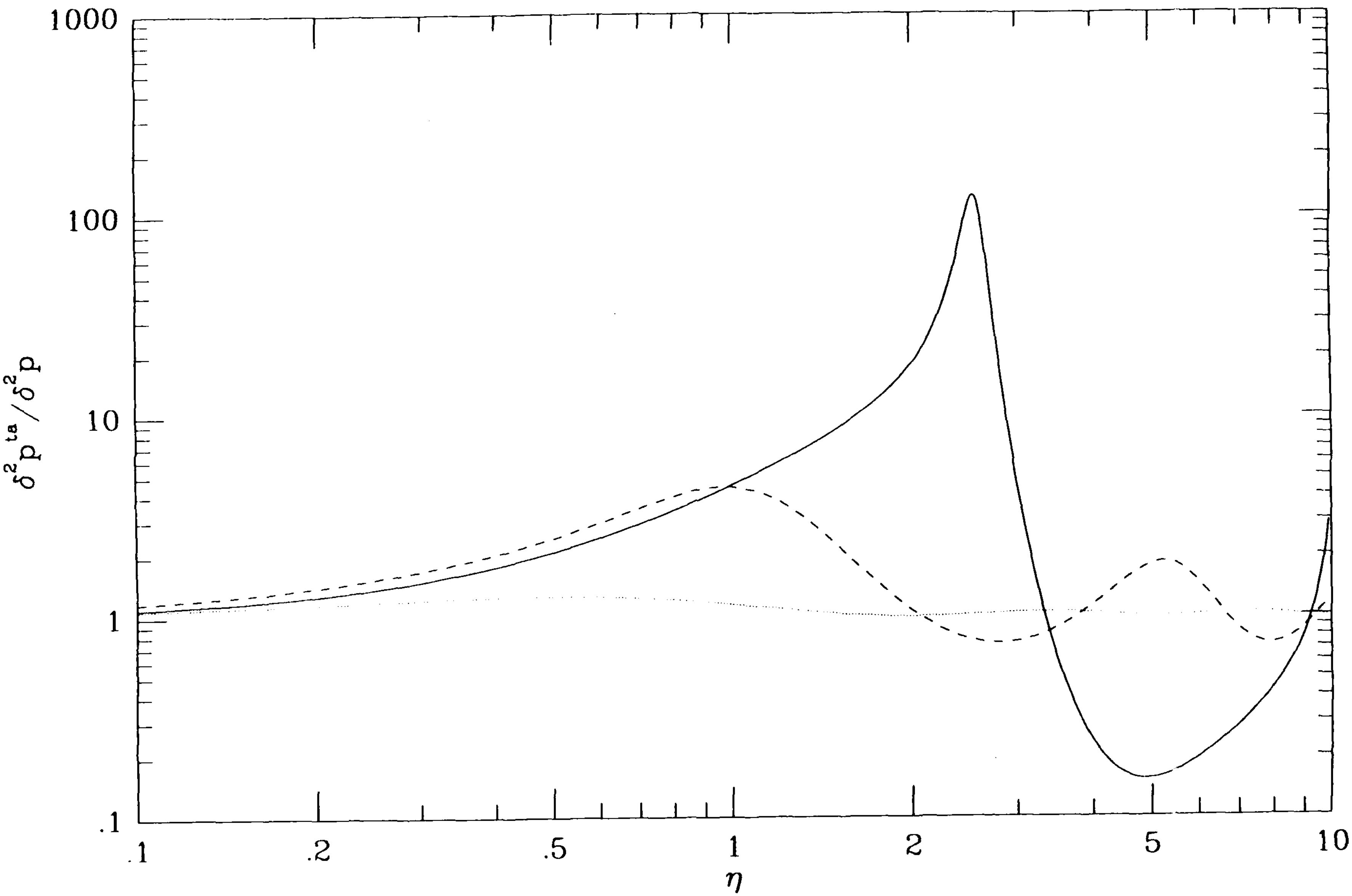


Figure 7



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